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OKSIDLANGAN MIS RUDASI TARKIBIDAGI MINERALLARNING QAYTA ISHLASH TEXNOLOGIYASINI TANLASHDAGI AHAMIYATI

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Annotatsiya. *Mis metaliga talabning oshishi, qayta ishlanishi qulay boʻlgan sulfidli mis rudalari zaxiralarining kamayishi oksidlangan, aralash tarkibdagi, balansdan tashqari mis rudalarini qayta ishlab kerakli komponentlarni ajratib olishga zarurat uygʻotmoqda. Lekin oksidlangan mis rudalarining murakkab mineralogik tarkibi, gidrofillik xususiyati qayta ishlashda qiyinchiliklar keltirib chiqaradi. Mazkur maqolada oksidlangan mis rudalari tarkibidagi mis minerallarining fizik-kimyoviy xususiyatlari, qayta ishlash texnologiyasini tanlashdagi ahamiyatlari, flotatsiyalanish qobilyatini oshirishda qoʻllanilishi mumkin boʻlgan reagentlar va gidrometallurgik qayta ishlash usullari tahlil qilingan.*

Kalit soʻzlar: *oksidlangan mis rudasi, misning oksidli minerallari, flotatsiya, sulfidlab flotatsiyalash, sulfidlovchilar, gidrometallurgiya.*

ЗНАЧЕНИЕ МИНЕРАЛЬНОГО СОСТАВА ОКИСЛЕННОЙ МЕДНОЙ РУДЫ ПРИ ВЫБОРЕ ТЕХНОЛОГИИ ПЕРЕРАБОТКИ

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Аннотация. *Рост спроса на медь и сокращение запасов сульфидных медных руд, удобных для переработки, вызывают необходимость переработки окисленных, смешанных по составу и забалансовых медных руд с целью извлечения необходимых компонентов. Однако сложный минералогический состав окисленных медных руд и их гидрофильные свойства создают трудности при переработке. В данной статье проанализированы физико-химические свойства медных минералов, содержащихся в окисленных рудах, их значение при выборе технологии переработки, возможные реагенты для повышения флотационной способности, а также гидрометаллургические методы переработки.*

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Ключевые слова: *окисленная медная руда, окисленные минералы меди, флотация, сульфидизация и флотация, сульфидизаторы, гидрометаллургия.*

THE IMPORTANCE OF THE MINERAL COMPOSITION OF OXIDIZED COPPER ORE IN THE SELECTION OF PROCESSING TECHNOLOGY

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Abstract. *The growing demand for copper and the depletion of easily processable sulfide copper ore reserves necessitate the processing of oxidized, compositionally mixed, and off-balance copper ores to extract valuable components. However, the complex mineralogical composition of oxidized copper ores and their hydrophilic properties present challenges in processing. This article analyzes the physicochemical properties of copper minerals contained in oxidized ores, their importance in selecting appropriate processing technologies, potential reagents for improving flotation performance, and hydrometallurgical processing methods.*

Keywords: *oxidized copper ore, oxidized copper minerals, flotation, sulfidization and flotation, sulfidizing agents, hydrometallurgy.*

Kirish. Rangli metall ishlab chiqarishga bo‘lgan talab oxirgi yillarda sezilarli darajada oshdi. Statistik ma’lumotlarga ko‘ra dunyo miqyosida mis metali iste’moli yiliga o‘rtacha 23-26 million tonnani tashkil etadi. Bunga sabab sifatida elektrotexnika hamda elektromobillar ishlab chiqarish xajmining keskin oshishi ko‘rsatilmoqda [1].

Mis metaliga talab yildan-yilga barqaror o‘sib bormoqda. London metall birjasida 2020-yil holatiga ko‘ra bir tonna mis narxi 6000-6500 AQSH dollari atrofida bo‘lgan bo‘lsa, 2025-yil birinchi choragiga kelib bu ko‘rsatkich 9100-9300 AQSH dollarini tashkil etdi [2]. Hozirgi vaqtda tasdiqlangan va qazib olinadigan mis zaxiralari 890 million tonna deb baholanmoqda. Mutaxassislar tomonidan olib borilgan tadqiqotlarga ko‘ra yangi konlar yoki mis ajratib olishning yangi texnologiyalari ishlab chiqilmasa ushbu zaxira 20 yilga yetadi [1].

An’anaviy sulfidli mis rudalaridan tashqari oksidli, aralash, balansdan tashqari mis rudalarini qayta ishlab, kerakli komponentlarni ajratib olish hozirgi kunning dolzarb masalalaridan hisoblanadi [3, 4, 5]. Lekin oksidli mis rudalarining gidrofillik xususiyati va murakkab mineralogik tarkibi sulfidli mis rudalarini qayta ishlashda qo‘llaniladigan ananaviy texnologiyalardan foydalanishda qiyinchilik tug‘diradi [6, 7].

Oksidlangan mis rudalari tarkibida mis karbonatlar – malaxit $CuCO_3 \cdot Cu(OH)_2$, azurit $2CuCO_3 \cdot Cu(OH)_2$, sulfatlar – xalkantit $CuSO_4 \cdot 5H_2O$, broshantit $CuSO_4 \cdot 3Cu(OH)_2$, antlerit $Cu_3(OH)_4SO_4$, xloridlar – atakamit $Cu_2Cl(OH)_3$, alyumosilikatlar va fosfatlar – biryuza $CuO \cdot 3Al_2O_3 \cdot 2P_2O_5 \cdot 9H_2O$, xrikozolla $CuSiO_3 \cdot nH_2O$, oksidlar – kuprit Cu_2O va tenorit CuO va boshqalar ko‘rinishida bo‘ladi [8, 9, 10].

Adabiyot tahlili va metodlar. Malaxit eng keng tarqalgan misning oksidli minerali bo‘lib, ruda tarkibida xalkotsit, azurit minerallari bilan birga keladi. Monoklinik kristal tuzilishga ega, unda misning ulushi 57,57 % ni tashkil etadi [11]. Xrikozolla ma’lum bir kimyoviy formulaga va tarkibga ega emas, odatda kristal holatdagi mis silikati va amorf dioksid aralashmasi sifatida tasniflanadi [12]. Kuprit odatda malaxit va xrikozolla bilan bog‘langan holatda keladi. Havoda oksidlanish natijasida tenoritga aylanishi oson, shuning uchun qayta ishlash vaqtida tenoritning xususiyatlarini namoyon qilishi mumkin [13].

Yuqorida ko‘rsatilgan adabiyotlarga tayanib shunday xulosaga kelish mumkinki, misning oksidli minerallari, shu jumladan malaxit, xrikozolla, kuprit

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sirt yuzasining yuqori gidrofillik xususiyati sababli ular suv yuzasida suzishga moyil emas, bu esa ananaviy flotatsiya jarayonini qo‘llashni murakkablashtiradi yoki butunlay ta’qiqlaydi. Malaxit aniq kristall tuzilishga ega bo‘lganligi sababli sulfidlovchilar yordamida yaxshi sulfidlanadi, xrikozolla yuzasi g‘ovakli bo‘lib kollektor adsorbsiyasida qiyinchilik keltirib chiqaradi, bu esa xrikozolla flotatsiyasini qiyinlashtiradi. Kuprit yuzasida malaxit va xrikozollaga qaraganda faol qatlam kamroq, lekin sulfidlash orqali sirt xususiyatini o‘zgartirish mumkin.

Hozirgi kunda oksidlangan mis rudalarini qayta ishlashda flotatsiya usuli keng qo‘llanilmoqda. Oksidli mis minerallarini flotatsiyalash to‘g‘ridan-to‘g‘ri yoki sulfidlab amalga oshirilishi mumkin [14]. To‘g‘ridan-to‘g‘ri flotatsiya yig‘uvchi, ko‘pik xosil qiluvchilardan foydalangan holda amalga oshirilsa, sulfidlab flotatsiyalash minerallarning sirt yuza xususiyatlarini o‘zgartirish uchun sulfidlovchilardan foydalanish orqali amalga oshiriladi [15, 16, 17, 18, 19].

Misning oksidli minerallarini to‘g‘ridan-to‘g‘ri flotatsiyalashda yig‘uvchi sifatida ksantogenat yaxshi samara bermaydi [20]. Xelat kollektori mis oksidi uchun yaxshi yig‘uvchi xususiyatga ega, aralash tarkibdagi rudalarda ham yaxshi samara beradi [21], lekin ularning kamchiligi selektivlik xususiyati yo‘q bo‘lib puch tog‘ jinslarini ham adsorbsiyalashi mumkin [22], mazkur tipdagi yig‘uvchilar bilan solishtirilganda natriy oleat kabi yog‘ kislotalari ham yig‘uvchi sifatida, ham iqtisodiy jihatdan samaraliroqdir [23]. Bundan tashqari gidroksamik kislota [24], oktil gidroksamik kislota [25], benzogidroksamik kislota [26] lar malaxitning gidrofoblik xususiyatini oshirib yaxshi flotatsiyalanishini ta’minlashi mumkin.

Tarkibi murakkab bo‘lmagan, yuqori navli oksidlangan mis rudalarini flotatsiyalashda to‘g‘ridan-to‘g‘ri usuldan foydalanish mumkin, ammo sanoatda, murakkab tarkibli, past sifatli rudalar uchun bu usul past selektivlik xususiyati, yuqori narxi, olingan konsentratdagi sifatning pastligi tufayli samarali emas deb baholanadi.

Sulfidlab flotatsiyalashda sulfidlovchilar yordamida mis oksidi minerallarining yuzasida mis sulfidlari hosil bo‘lishi hatto sulfidli qobiq hosil bo‘lishi mumkin, shu sababli mis oksidi minerali mis sulfidi kabi xususiyatga ega bo‘ladi, natijada yaxshi flotatsiyalanadi [27]. Mis oksidi minerallarini sulfidlash jarayonida sulfidlanish natijalariga ko‘plab omillar ta’sir qilishi mumkin. Masalan, mineral sirtining strukturaviy xususiyatlari, sulfidlovchi reagent turi va dozasi, sulfidlanish vaqti, pH muhiti, harorat va boshqalar [28, 29, 30].

Sulfidlovchilar sifatida oltingugurt, ammoniy sulfid, natriy sulfid, natriy gidrosulfid, natriy polisulfidlar keng qo‘llaniladi [31, 32, 33]. Natriy gidrosulfid misning flotatsiya samarali sulfidlovchi, natriy gidrosulfid bilan ammoniy sulfidining 1:1 aralashmasidan foydalanish flotatsiya samaradorligini sezilarli darajada oshirgan [34].

Sulfidlovchi reagent miqdori to‘g‘ridan-to‘g‘ri jarayonga ta’sir ko‘rsatadi, dozani sozlash orqali mis oksidi flotatsiyasini faollashtirishi yoki susaytirishi mumkin. Yetarli bo‘lmagan miqdor mineral yuzasida yetarlicha sulfid pardani hosil qilmaydi, ortiqcha miqdor esa yig‘uvchi reagent sarfini oshirishi mumkin [33].

Sulfidlanish vaqti mineral yuzasida sulfid parda qoplanishi va intensivligiga ta’sir qiladi, agar vaqt juda qisqa bo‘lsa sulfidlanish darajasi yetarli bo‘lmaydi, agar sulfidlanish vaqti uzoq kechsa sulfidlovchining ta’siri pasayadi, natijada sulfid parda mineral yuzasidan tushib ketadi va minerallar yaxshi flotatsiyalanmaydi [35].

Oksidli mis minerallari flotatsiyasida pH 8-10 da malaxitning sulfidlanishi va suzuvchanligi yaxshi bo‘ladi [36], kislotali muhitda ksantogenatlar parchalanadi [37]. Agar pH 10 dan yuqori bo‘lsa gidroksid ionlari hosil bo‘lishi kuchayadi va malaxitning ksantogenatga adsorbsiyasini susaytiradi. Mis oksidlari uchun flotatsiya muhiti 9-9,5 eng yaxshi ko‘rsatkich hisoblanadi [38].

Sulfidlash haroratining oshishi sulfidlanish darajasi va samaradorligini oshiradi, biroq yuqori harorat ishlab chiqarish xarajatlari oshishiga, flotamashina va atrof-muhit muammolariga olib kelishi mumkin [39].

Sulfidlab flotatsiyalashda pulpada hosil bo‘lgan ortiqcha sulfidlar jarayonda yig‘uvchi reagent bilan raqobatlashadi, ya’ni yig‘uvchi reagentning mineral yuzasiga yopishishiga to‘sqinlik ko‘rsatadi, bu flotatsiya samaradorligiga salbiy ta’sir ko‘rsatadi. Shu sababli jarayonda maqbul parametrlarni – sulfidlovchi miqdori, vaqt, pH ko‘rsatkich, harorat va boshqalarni to‘g‘ri tanlash muhim hisoblanadi.

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Sulfidlab flotatsiyalashda faollashtiruvchi reagentlardan foydalanish minerallar yuzasida faol joylar hosil bo‘lishiga va yig‘uvchi reagentning yaxshi adsorbsiyasiga sabab bo‘ladi. Faollashtiruvchilar sifatida a-benzoin oksim, antranilik kislota, kupferron, N-benzoil-N-fenilgidroksilamin, 8-gidroksixinolinlarni qo‘llash xrikozollar flotatsiyasida yaxshi natija ko‘rsatgan [40, 41]. Bundan tashqari 1H-Benzotriazol oksidli mis minerallarini sulfidlab flotatsiyalashda yaxshi faollantiruvchi ta’sir ko‘rsatadi, minerallarning sirt barqarorligini oshiradi, yig‘uvchi reagent adsorbsiyasi uchun qulay sharoit ta’minlaydi [42].

Oksidli mis minerallari uchun faollashtiruvchi sifatida ammoniy / amin tuzlarini qo‘llash sulfidlanish muhitini yaxshilashi, minerallar yuzasida faol joylar sonini oshirishi va sulfidlanishni kuchaytirishi mumkin. Bundan tashqari ammoniy tuzi sulfid ionlarining salbiy ta’sirini kamaytirish uchun pulpada bufer bo‘lib qatnashishi mumkin [43]. Etilendiamin fosfat minerallarda sulfidlovchi va yig‘uvchilar adsorbsiyasi tezligini oshirib jarayonni tezlashtirishi mumkin [44]. Bundan tashqari etilendiamin fosfat jarayonda puch tog‘ jinslarining birikishi va cho‘kishini tezlashtiradi [45].

Vodorod peroksid yordamida kuprit yuzasini modifikatsiya qilish va uning sulfidlanish qobiliyatini oshirish imkoni mavjud [46]. Mis oksidini sulfidlab flotatsiyalashda natriy butil ksantat (NaBX) va dodetsilamin (DDA) kombinatsiyalangan kollektor sifatida foydalanilgan. Tadqiqot natijalariga ko‘ra NaBX va DDA birgalikda ishlatish pH 7-11 oralig‘ida faqat NaBX dan foydalanishga qaraganda samaraliroq, NaBX va DDA ning optimal molyar nisbati 2:1. NaBX+DDA miqdori (100+54) g/t bo‘lganda misning tiklanishi 15,93% dan 76,73% ga oshgan [47].

Xulosa qilib aytganda oksidlangan mis minerallarini flotatsiyalash hozirgi kunda keng tarqalgan va samaradorligi yuqori usullardan biri. Lekin oksidli mis minerallarining yuqori sirt gidrofillik xususiyati hamda murakkab mineralogik tarkibi tufayli to‘g‘ridan-to‘g‘ri flotatsiyalash yaxshi natija bermaydi. Jarayonda sulfidlovchilar yordamida sulfidlab flotatsiyalashdan foydalanish ya’ni oltingugurt, natriy sulfid, ammoniy gidrosulfid, natriy gidrosulfid va shu kabi sulfidlovchilar yordamida mineral yuzalarida sulfid qatlam hosil qilish orqali minerallarning gidrofoblik xususiyatini oshirish keng foydalanilayotgan, iqtisodiy samara berayotgan usul hisoblanadi.

Oksidlangan mis rudalarini qayta ishlashning yana bir samarali usullaridan biri bu gidrometallurgik qayta ishlash hisoblanadi. Gidrometallurgik qayta ishlashda uyumda tanlab eritish, bakteriyalar yordamida tanlab eritish, avtoklavda tanlab eritish amaliyotda keng qo‘llanilgan [48, 49].

Bakteriologik tanlab eritishda T.ferrooxidans-atsidofil tiobatsillalardan foydalanilgan. Oksidlangan mis rudasi, oltingugugurt, xalkopirit nisbati 1:1:1, oksidlangan mis rudasiga oltingugurt va xalkopirit aralashtirilganda misning erish darajasi 61% ga yetgan [50]. Erituvchi sifatida organik kislota ($C_4H_6O_6$, tartarik kislota) dan foydalanilganda tadqiqot natijalari tanlab eritish jarayonida ushbu organik reagentning samaradorligini, tejamkorligini va ekologik tozaligini ko‘rsatadi. Ruda 0,074 mm gacha yanchilgan, organik kislota konsentratsiyasi 0,2 mol/l, jarayon davomiyligi 60 daqiqa, S:Q nisbati 1:10, harorat 25 ^{o}C, aralashtirish tezligi 300 ayl/min, misning eritmaga ajralishi 73,18%. Tartatik kislota yordamida malaxitdan misni tanlab eritish an’anaviy kislotalarga qaraganda ekologik toza va iqtisodiy samaradorligi isbotlangan [51]. Tanlab eritishda etilendiaminetrasirka kislotasining (EDTA·2Na) dinatriyli tuzining suvli eritmasidan foydalanilganda reagent konsentratsiyasining oshishi jarayon tezligini oshirgan, S:Q nisbati jarayon tezligiga sezilarli ta’sir ko‘rsatmagan [52]. Shuningdek ammiak sulfati yordamida tanlab eritishda eritmada mis – 1,24 g/l, misning ajralish darajasi – 87,96% ni ko‘rsatgan. Mazkur usul kombinatsiyalangan flotatsion va tanlab eritish jarayonining amaliyotda qo‘llash imkoniyatini ko‘rsatadi. Misni ammiak sulfati bilan tanlab eritish nafaqat ekologik, balki iqtisodiy jihatdan ham samarali usul bo‘lib, yuqori regeneratsiya va sifatli mahsulot olish imkonini beradi [53]. Bundan tashqari sianid eritmasi [54] va sulfat kislota [55] oksidlangan rudalar uchun yaxshi erituvchi hisoblanadi.

Natijalar va muhokama. Hozirgi kunda chuchuk suv resurslaridan oqilona foydalanish maqsadida dengiz suvi yoki sho‘r suvni qo‘llagan holda tanlab eritish jarayonlarini amalga oshirish ishlari o‘rganilmoqda. Bu usul mikrobiologik faoliyatni oshirish va chuchuk suv sarfini kamaytirish imkonini beradi. Kalsiy xlorid eritmasi yordamida

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tanlab eritishda misning ajralishi 99% ga yetgan, kalsiy xlorid konsentratsiyasi 110-165 g/l, zarracha oʻlchamini 15 mikronga yetkazish mis ajralishini 0,2, temir ajralishini 2% ga oshirgan. Erituvchi sifatida xlorid-sulfat eritmasidan foyda-lanilganda xlorid jarayonda katalizator sifatida ishtirok etgan, yuqori konsentratsiyali xlorli oqova suvlari orqali past sifatli, aralash tarkibdagi mis rudalarini tanlab eritish boʻyicha olib borilgan tadqiqotlarda harorat 80°C, davomiyligi 4 soat, misni ajralish darajasi – 89,46% ga yetgan.

“Olmaliq KMK” AJ Qalmoqir koni oksidlangan mis rudalarini 92-95% puch togʻ jinslari tashkil etadi, ularning asosiy qismi kvars, dala shpati, qisman muskovit, xlorit, biotit, magnetit, apatit va boshqalar. Ruda minerallari esa 3-8% ni tashkil etib asosan kvars tomirlari bilan uchraydi. Ruda tarkibida mis malaxit, kuprit, xalkozin, kovellin, bornit, kubanit va xalkopirit koʻrinishida uchraydi, bunda malaxitning ulushi koʻproq (1-jadval).

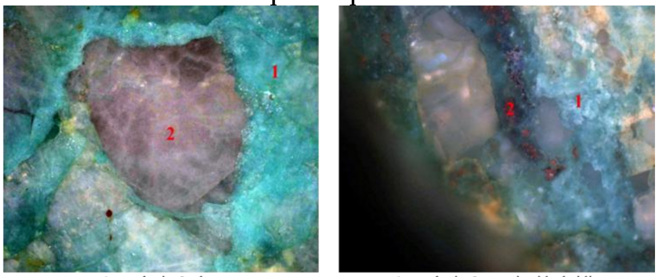
1-jadval

“Olmaliq KMK” AJ Qalmoqir koni oksidlangan mis rudasi tarkibida misning minerallarda taqsimlanishi

Mineral	Misning ulushi, %
Xalkopirit	15,90
Bornit	3,85
Kovellin-xalkozin	19,55
Qoʻshimcha sulfidlar	2,71
Mis karbonatlari	19,96
Mis sulfatlari	8,99
Xrikozolla va bogʻlangan mis	18,70
Psevdomalaxit	3,76
Turkuz	0,60
Kuprit	0,31
Oksidlar / Gidroksidlar (*Fe*)	5,66
Jami:	100,00

Malaxit tomirlar, toʻplamlar shaklida uchraydi, tomirlar tosh yoriqlari boʻylab rivojlangan va temir gidroksidlari bilan birga kelgan (1-rasm). Malaxitning zarracha oʻlchami oʻrtacha 0,02-0,5 mm.

“Olmaliq KMK” AJ Qalmoqir koni oksidlangan mis rudasining asosini kvars minerali tashkil etib misning katta qismi malaxit koʻrinishida tarqalgan. Malaxit rudada kvars hamda temir gidroksidi bilan bogʻlangan holatda uchraydi. Yuqoridagi adabiyotlarda keltirilgan ma’lumot-lardan kelib chiqqan holda shunday xulosaga kelish mumkinki, bunday shakldagi malaxitni flotat-siyalanishini ta’minlashda yigʻuvchi reagent sifa-tida natriy oleat yaxshi samara beradi. Oktil gidroksamat va kerosin aralashmasi malaxitning temir gidroksid bilan birgalikdagi koʻrinishida yaxshi natija koʻrsatadi, jarayonda kerosinning bir me’yorda taqsimlanishi uning malaxit yuzasida tarqalishini ta’minlaydi, bu esa uning gidrofoblik xususiyatini oshiradi. Ammoniy sulfid va natriy sulfidning mos ravishda malaxitning sulfidlanishiga ta’siri oʻrganilganda ammoniy sulfid ionlari boʻlgan malaxit natriy sulfid ionlari boʻlgan malaxitga qaraganda yuqori flotatsiya natijalarini koʻr-satganini hisobga olib ammoniy sulfidni yaxshi sulfidlovchi sifatida qabul qilish mumkin.



1 - malaxit, 2 - kvars   1 - malaxit, 2 - temir gidroksidi

1-rasm. Malaxitning temir gidroksidi va kvars bilan birgalikdagi koʻrinishi.

Xulosa. 1-jadvaldan koʻrinadiki, ruda tarkibidagi misning 40-42% i sulfid koʻrinishida, 58-60% i oksidlangan holatda. Bunday aralash, murakkab tarkibdagi rudani qayta ishlashda faqat flotatsiya yoki gidrometallurgiya usulidan foydalanish yetarli natija bermaydi, kombinatsiyalangan usuldan foydalanish mis va boshqa kerakli komponentlarni ajratib olish imkoniyatini oshiradi.

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